FILE COPY

NWC TP 6984

AD-A213 424

Attempted Synthesis of 1,4-Dinitro[3,4-b]-[3,4-e]Difurazanopiperazine

by
John W. Fischer
Charlotte K. Lowe-Ma
Robin A. Nissan
Richard A. Hollins
and
Ronald L. Atkins
Research Department

JULY 1989

NAVAL WEAPONS CENTER
CHINA LAKE, CA 93555-6001

SELECTE
SEP 28 1989
S D

Approved for public release; distribution is unlimited.

89 9 28 093

Naval Weapons Center

FOREWORD

Predictions are that present day propellants and explosives will not meet the demands of the future. To meet this proposed threat, there is a continuing effort at the Naval Weapons Center to synthesize new energetic materials that exceed 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraaza-cyclooctane (HMX) in performance and insensitivity. As a contribution to this program, the synthesis of a promising candidate, 1,4-dinitro-[3,4-b]-[5,6-e]difurazano-piperazine, was undertaken. This report describes the various synthetic routes attempted which led to precursors of the desired target compound.

This report has been reviewed for technical accuracy by Arnold T. Nielsen and William S. Wilson.

Approved by
R. L. DERR, *Head*
Research Department
18 July 1989

Under authority of
J. A. BURT
Capt., USN
Commander

Released for publication by
G. R. SCHIEFER
Technical Director

NWC Technical Publication 6984

Published by ..... Technical Information Department
Collation ..... Cover, 16 Leaves
First printing ..... 115 Copies

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION: UNCLASSIFIED	1b RESTRICTIVE MARKINGS
2a SECURITY CLASSIFICATION AUTHORITY	3 DISTRIBUTION AVAILABILITY OF REPORT: Approved for public release; distribution is unlimited.
2b DECLASSIFICATION / DOWNGRADING SCHEDULE	
4 PERFORMING ORGANIZATION REPORT NUMBER(S): NWC TP 6984	5 MONITORING ORGANIZATION REPORT NUMBER(S)
6a NAME OF PERFORMING ORGANIZATION: Naval Weapons Center; 6b OFFICE SYMBOL (If applicable)	7a NAME OF MONITORING ORGANIZATION
6c ADDRESS (City, State, and ZIP Code): China Lake, CA 93555-6001	7b ADDRESS (City, State, and ZIP Code)
8a NAME OF FUNDING / SPONSORING ORGANIZATION: Office or Naval Research; 8b OFFICE SYMBOL (If applicable)	9 PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c ADDRESS (City, State, and ZIP Code): Arlington, VA 22217	10 SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO 61153N; PROJECT NO BR02402; TASK NO BR02402; WORK UNIT ACCESSION NO 138509

11 TITLE (Include Security Classification)

ATTEMPTED SYNTHESIS OF 1,4-DINITRO[3,4-b]-[3,4-e]DIFURAZANOPIPERAZINE

12 PERSONAL AUTHOR(S)

John W. Fischer, Charlotte K. Lowe-Ma, Robin A. Nissan, Richard A. Hollins, Ronald L. Atkins

13a TYPE OF REPORT	13b TIME COVERED	14 DATE OF REPORT (Year, Month, Day)	15 PAGE COUNT
Final	FROM 84 Aug TO 88 Aug	1989, July	30

16 SUPPLEMENTARY NOTATION

17 COSATI CODES		
FIELD	GROUP	SUB-GROUP
19	01	

18 SUBJECT TERMS (Continue on reverse if necessary and identify by block number)

1,4-Dinitro-[3,4-b]-[5,6-c]difurazanopiperazine, Energetic material, Furazan, Nitramine

19 ABSTRACT (Continue on reverse if necessary and identify by block number)

The synthesis of 1,4-dinitro-[3,4-b],[5,6-e]difurazanopiperazine (CL-X) was attempted. Condensation of the dilithio anions of N,N'-disubstituted-diaminofurazans with cyanogen oxide gave 1,4-disubstituted-[3,4-b]furazano-5,6-dioximinopiperazines. Ring closure with sodium hydroxide in ethylene glycol at 150°C for 2 hours yielded 1,4-disubstituted-[3,4-b],[5,6-e]difurazanopiperazines. Attempts to convert these precursors into CL-X is described. A successful synthesis of CL-X was not achieved.

20 DISTRIBUTION / AVAILABILITY OF ABSTRACT: ☒ UNCLASSIFIED UNLIMITED ☐ SAME AS RPT ☐ DTIC USERS	21 ABSTRACT SECURITY CLASSIFICATION: UNCLASSIFIED
22a NAME OF RESPONSIBLE INDIVIDUAL: John W. Fischer	22b TELEPHONE (Include Area Code): 619-939-1641; 22c OFFICE SYMBOL: 3853

DD FORM 1473, 84 MAR — 83 APR edition may be used until exhausted. All other editions are obsolete.

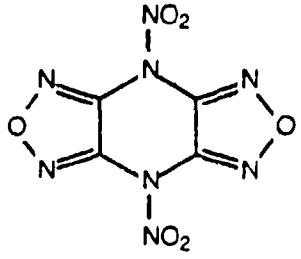
☆ U.S. Government Printing Office 1986--607-044

Accession For
NTIS GRA&I
DTIC TAB
Unannounced
Justification
By
Distribution/
Availability Codes
Dist | Avail and/or Special
A-1

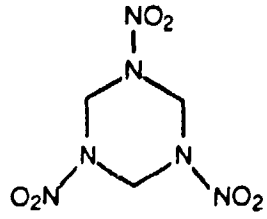
CONTENTS

INTRODUCTION

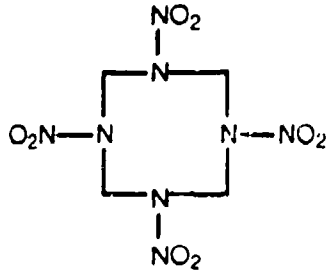
Predictions are that present day explosives and propellants will fail to meet future battlefield demands. As both aerial and ground targets become more difficult to defeat, a new generation of energetic materials will be needed. These new compounds will have to exceed 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX) in performance while still remaining insensitive. Energetic materials which are hazardous to handle and sensitive to external stimuli will be of little value in the dangerous battlefield environment. Because large quantities of explosives and propellants are stored and handled in the close confines of a ship, the problem of sensitivity is especially important to the Navy. In an effort to meet these requirements, we chose to investigate the synthesis of 1,4-dinitro-[3,4-b]-[3,4-e]-difurazanopiperazine (1) with the predicted properties as compared to RDX and HMX (Reference 1).



1



RDX



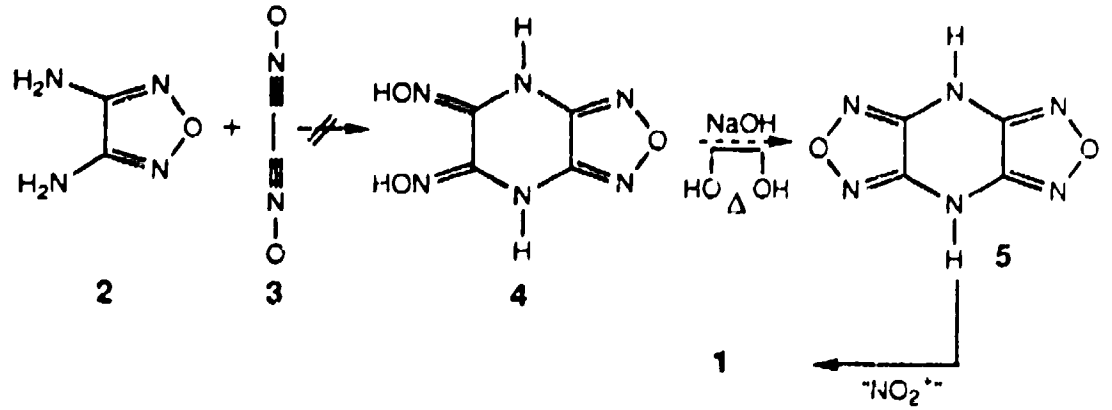
HMX

	1	RDX	HMX
Density (g/cc)	2.00	1.82	1.90
Detonation velocity (km/s)	9.7	8.75	9.15
Detonation pressure (Kbar)	450	390	393
Isp (s)	266	...	264

RESULTS AND DISCUSSION

We initially envisioned the construction of this linearly fused tricycle (1) to start with the reaction of 3,4-diaminofurazan (2) and cyanogen oxide (3) (Reference 2) to give the dioximinofurazanopiperazine (4). Ring closure (Reference 3) utilizing sodium hydroxide in ethylene glycol at 150°C was expected to

SCHEME 1

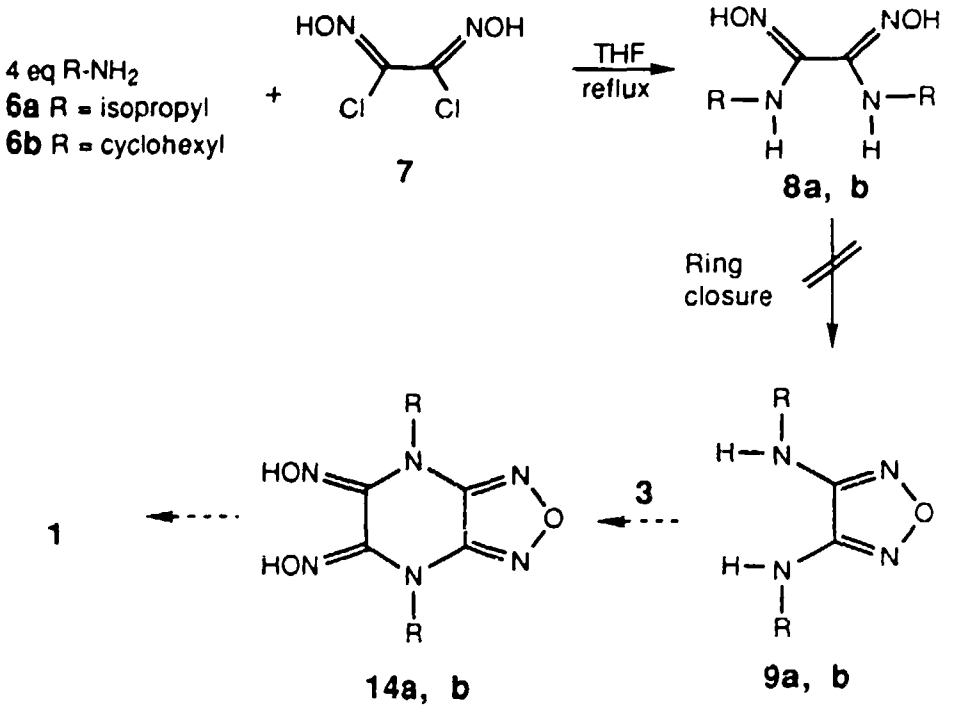


2 3 4 5 1

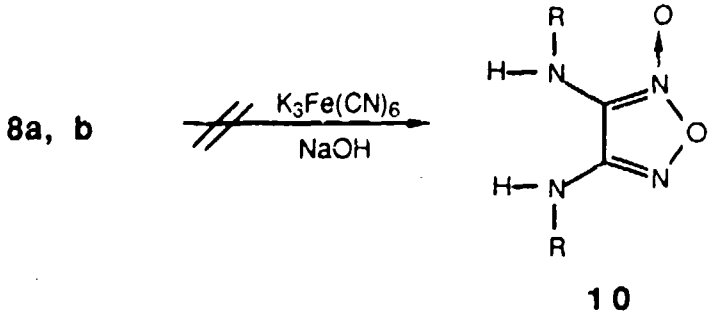
yield 5 (Scheme 1). Nitration of amine 5 would give 1. The condensation reaction of 2 and 3 failed, presumably due to the poor nucleophilic character of the electron-deficient amine nitrogens of 2 (Reference 4). An attempt to generate the dilithio anion of 2 by treatment with either n-butyl lithium or tert-butyl lithium followed by treatment with cyanogen oxide also failed to produce any of the desired condensation product 4.

The strong electron withdrawing nature of the furazan moiety greatly reduces the reactivity of the amine nitrogens. We believed that if an electron-donating alkyl group, such as isopropyl or cyclohexyl were attached, the nucleophilicity of these nitrogens would be increased. To this end (Scheme 2), we treated the appropriate amines (6a and b) (References 2 and 3), with dichloroglyoxime (7) in refluxing tetrahydrofuran (THF) giving the corresponding substituted diaminoglyoximes (8a and b) in near quantitative yields. Ring closure of 8a or b would give the activated diamino-furazans 9a and b. Compounds of type 9 would be transformed into 1 following a similar series of reactions as outlined in Scheme 1. Unfortunately, the desired dehydrative ring closure of 8 did not occur. Dioximes 8a and b failed to close to furazans 9 using a

SCHEME 2

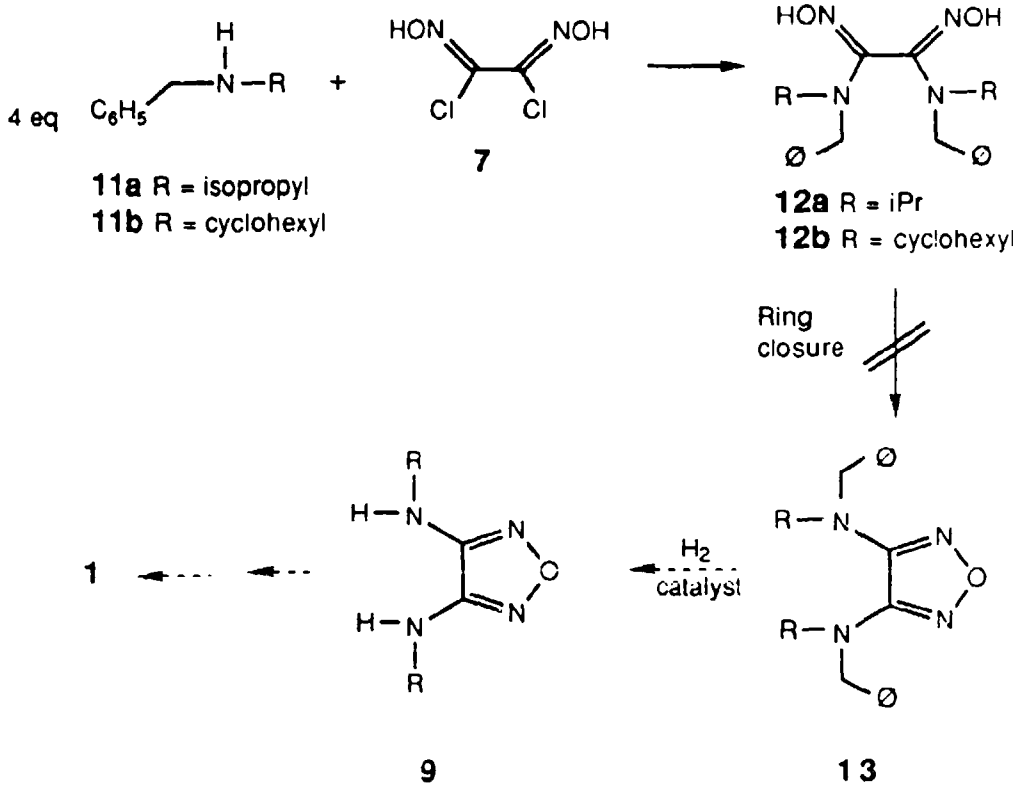


variety of dehydrative conditions, i.e., NaOH at 150°C, dicyclohexylcarbodiimide, or P_2O_5. Attempts to convert **8** to furoxans (**10**) using potassium ferricyanide (Reference 3) also proved fruitless.

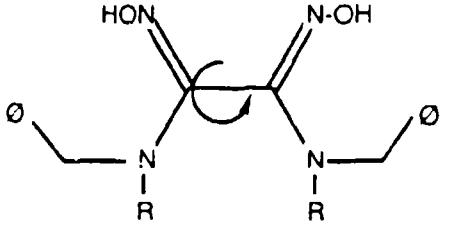


Literature reports claim successful furazan and furoxan formation of this type only when the amine nitrogens of diaminoglyoximes were fully substituted (Reference 3). No explanation was given for these results. To circumvent this problem, we attached benzyl groups to the amine nitrogens, which, after ring closure, could be removed by hydrogenolysis (Reference 5) (Scheme 3). Dichloroglyoxime (7)

SCHEME 3



was treated with the substituted amines (**11a** and **b**) in refluxing THF to yield the fully substituted diaminoglyoximes (**12a** and **b**). Ring closure to **13**, employing the methods described above, again failed. The probable reason for this lack of reactivity is severe steric congestion hindering rotation about the bond between the two oxime functionalities. Before furazan or furoxan formation can occur, the oximes must achieve



coplanarity. ^{13}C and ^{1}H NMR show a much more complicated set of signals than anticipated. In **12a** the isopropyl methyls appear as a doublet of doublets and the benzyl methylenes as an AB quartet (see Experimental Section). Figure 1 shows the benzyl methylenes ^{1}H signal at various temperatures. Even at 140°C, the signal is quite broad. If there were the necessary rotations about all bonds, all four benzyl protons would appear as a sharp singlet. The NMR data indicated that this molecule adopts a rigid

conformation which precludes rotation about the central σ bond rendering it inert to furazan or furoxan formation.

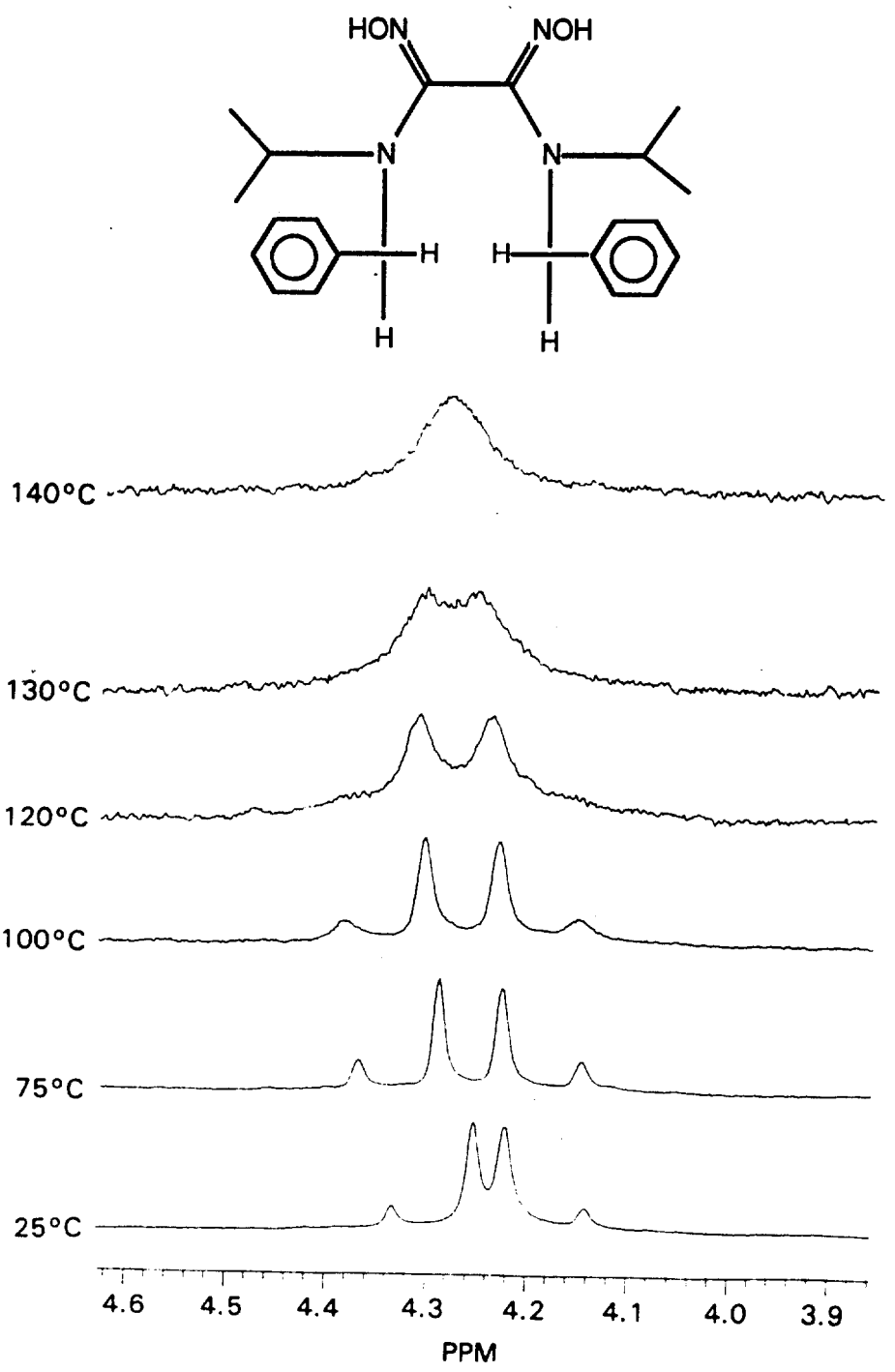
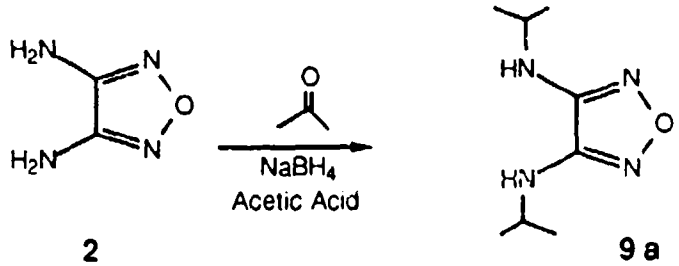


FIGURE 1. Variable Temperature Study of Benzyl Protons of Compound **12a**.

Using a shorter, although inefficient method, we were able to form **9a**. Diaminofurazan (**2**), upon treatment with a mixture of acetone and sodium borohydride

in acetic acid (Reference 6) yielded modest amounts of N,N'-diisopropyl-3,4-diaminofurazan (**9a**).

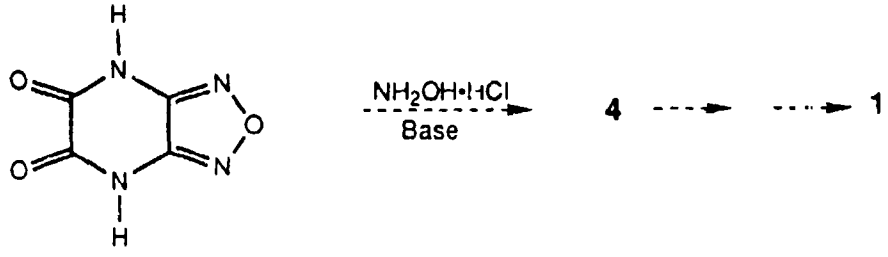


2 **9a**

Similar reaction with cyclohexanone gave **9b** but only in very low yield after extensive purification. Much to our dismay, however, direct reaction of **9a** and cyanogen oxides failed to give any trace of **14a**. Addition of sodium bicarbonate, sodium carbonate, or sodium hydroxide did not induce reaction. The addition of an electron-donating alkyl group did not sufficiently activate the amine nitrogens.

A new synthetic method was examined (Scheme 4). The α-diketofurazanopiperazine (**15**) is available from the condensation of oxalic acid and **2** (Reference 7).

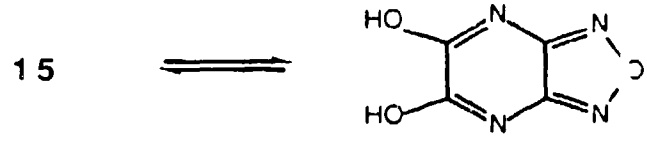
SCHEME 4



15

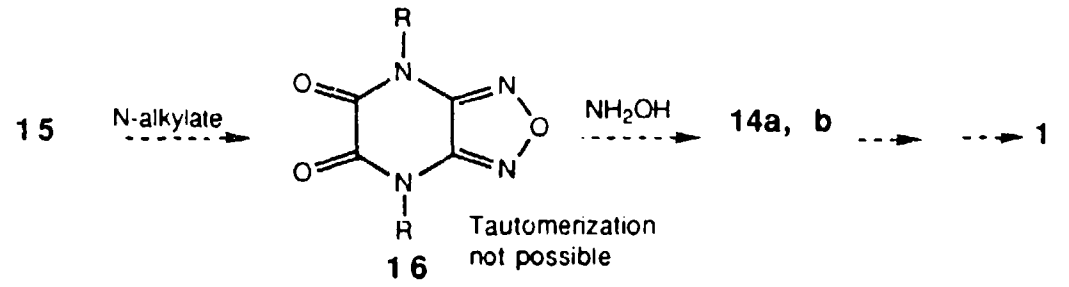
Treatment of **15** with hydroxylamine was expected to give the dioxime **4** which would then be converted to **1**. Unfortunately, even under very forcing conditions, a large excess of hydroxylamine hydrochloride, base, prolonged reaction times, and elevated temperatures, no evidence of desired oxime formation was seen.

Gasco and coworkers report that **15** exists as a pair of tautomers in equilibrium (Reference 7). Under the conditions used for oxime formation, it may be

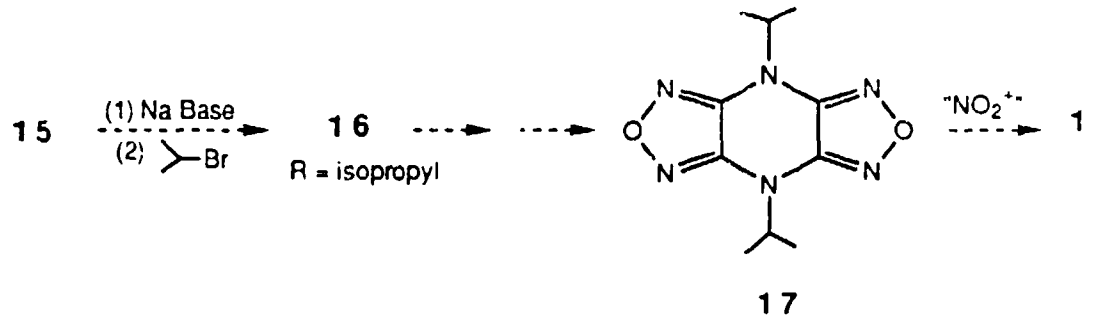


that the equilibrium shifted exclusively to the right rendering the molecule inert. If this tautomerization could be blocked by affixing an appropriate group to the piperazine nitrogens, we believed it could then be possible to form the desired oxime as outlined in Scheme 5. Amides are known to N-alkylate (Reference 8) if treated first with a sodium

SCHEME 5

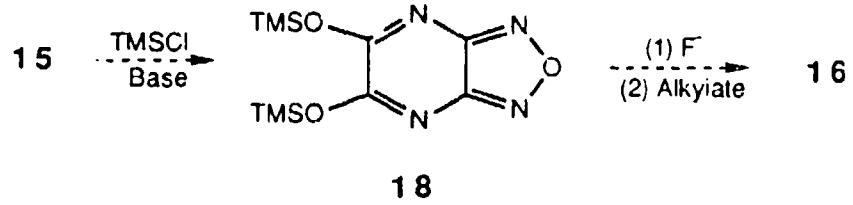


base followed by an alkylating agent. Alkylation of **15** was attempted by generation of the disodium salt and subsequent addition of isopropyl bromide. We chose the isopropyl



group because if **16** could be converted to **17**, the isopropyl appendages could then possibly be nitrolyzed off (Reference 9) to give **1**. The bases tried were sodium amide, sodium bicarbonate, and sodium hydroxide. Upon acidic workup, only unreacted **15** was recovered.

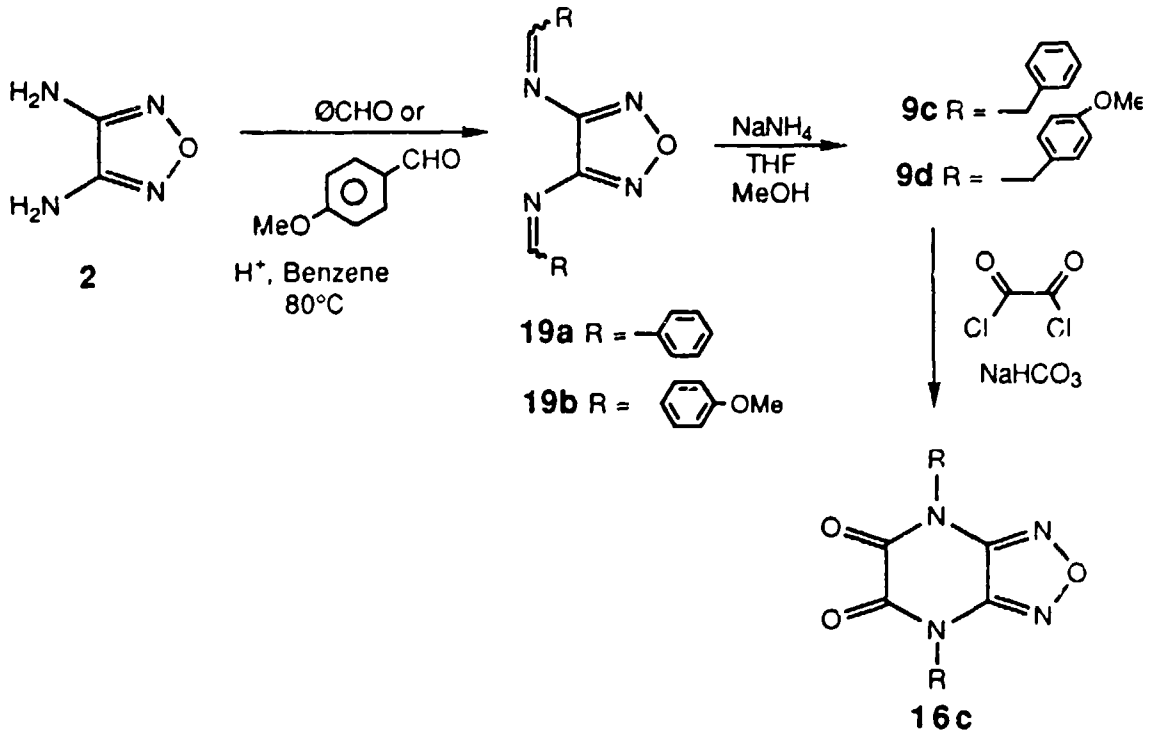
We next attempted to silylate **15** using trimethylsilyl chloride and imidazole or triethylamine. If silyl enol ether (**18**) were treated with fluoride, N-alkylation may



have been possible. No silyation was observed. In every attempt, only unreacted starting material was recovered.

We turned our attention to a new approach to **16** (Scheme 6). Diaminofurazan (**2**), upon treatment with benzaldehyde or p-anisaldehyde in refluxing benzene

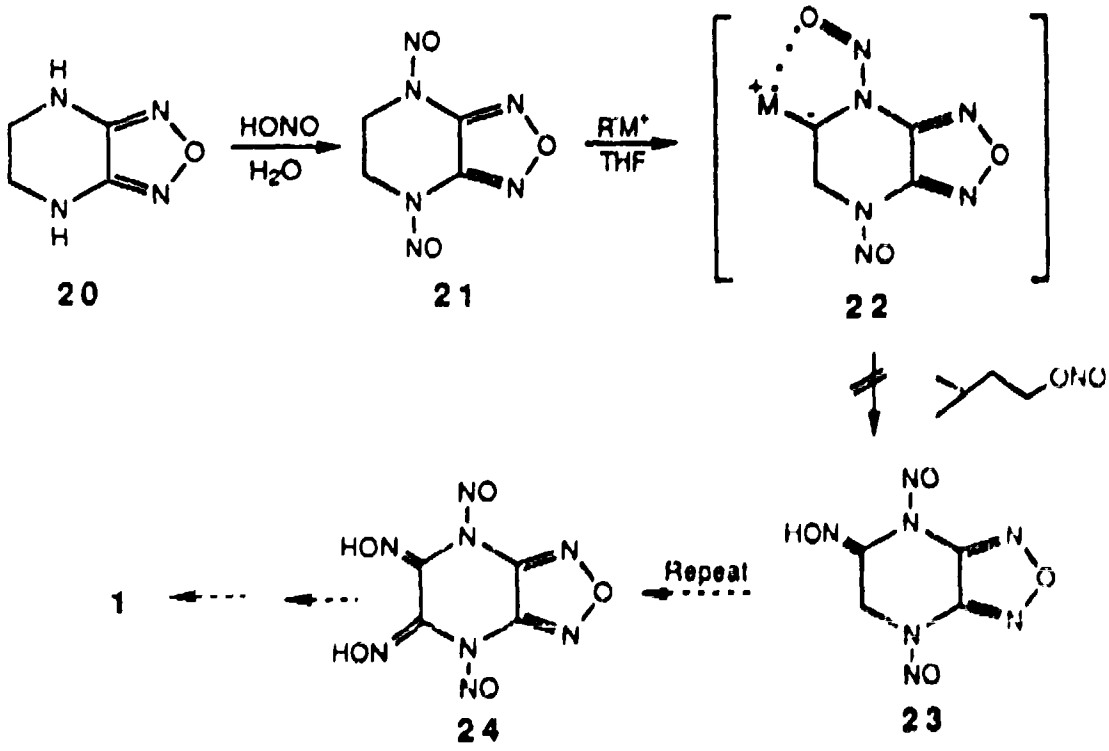
SCHEME 6



containing a catalytic amount of p-toluene sulfonic acid (Reference 10), gave the unstable imine (**19**), which was reduced (Reference 10) *in situ* with sodium borohydride to **9c** and **d**. Using high dilution/slow addition techniques, **9c** was condensed with oxalyl chloride (Reference 12) to yield the desired disubstituted diamide (**16c**). The benzyl group was chosen because it was seen as being more versatile than the isopropyl functionality. Whereas the isopropyl group was viewed as a nitrolyzable entity, a benzyl group was thought to be not only nitrolyzable but also removeable by catalytic hydrogenation (functioning as a protecting group) eventually yielding the free amine **5**. With no tautomerization possible, **16** was treated with hydroxylamine. No oxime formed. Again, using the forcing conditions discussed above, only unreacted starting material was isolated. Comparable reactions with **9a** and **9d** were not attempted.

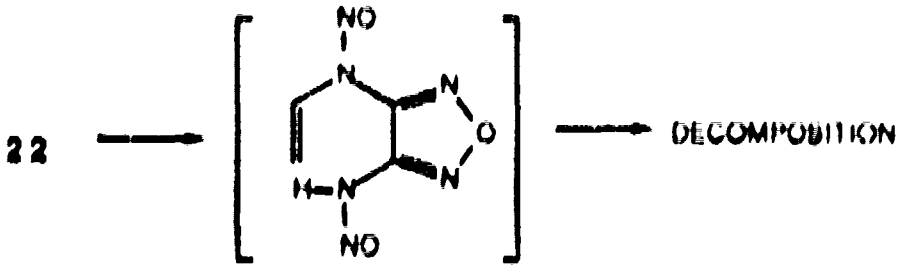
After this disappointing result, a longer synthetic route was investigated (Scheme 7).

SCHEME 7



This strategy employs generation of an anion (22) α to a stabilizing nitrosamine (Reference 13). The anion would then be treated with isoamyl nitrite to form the oxime 23. Protection of the oxime followed by a repeat of the base and isoamyl nitrite treatment was predicted to give the 1,2-dioxime (24). Ring closure of 24 and nitrolysis or oxidation of the nitroso groups would yield nitramine (1).

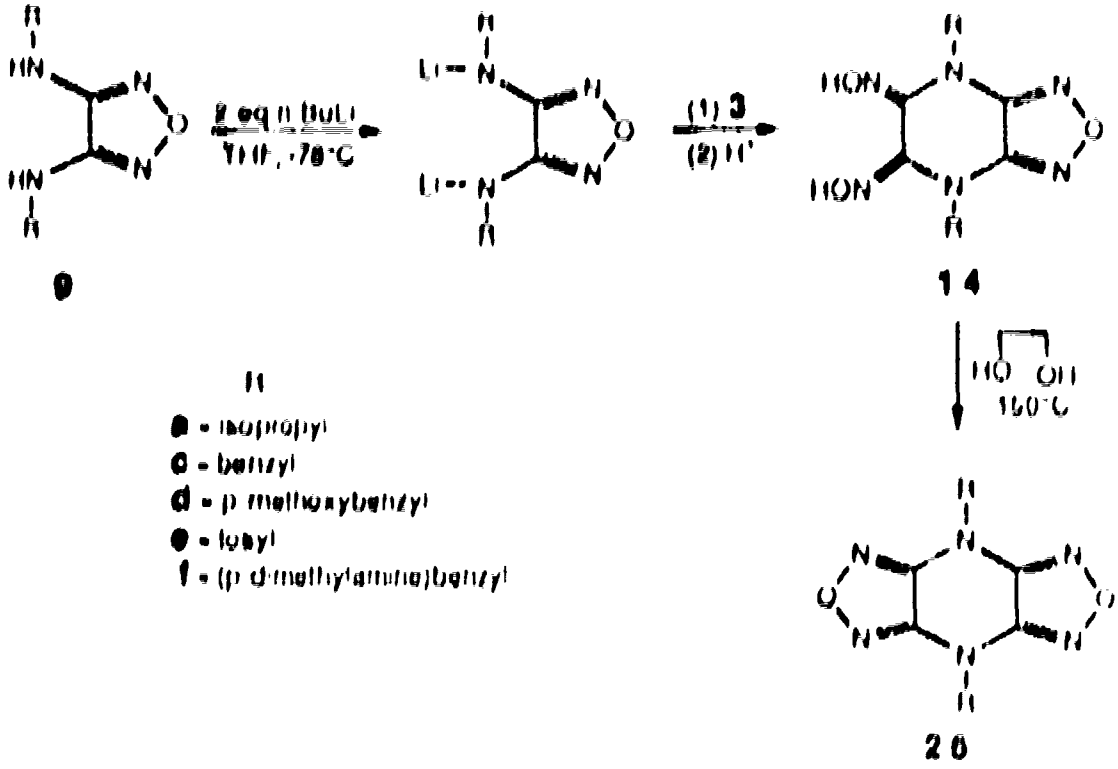
Furazanopiperazine (20) (Reference 2b and c) when treated with an excess of nitrous acid gave dinitrosopiperazine 21. We were confident that generation of the anion α to the nitrosamine functionality of 22 was accomplished using a variety of bases, i.e., lithium diisopropyl amide, lithium hexamethyl-disilazide, or potassium hexamethyldisilazide (Reference 13c). However, the anion is very stable and inert to electrophilic attack by isoamyl nitrite to form oxime 23. Attempts to unmask the anion with combinations of THF, hexamethylphosphoramide (HMPA), and tetramethylmethylenediamine (TMEDA) failed to induce the desired react If THF, HMPA, TMEDA, a large excess of isoamyl nitrite, and elevated temperatures were used, the reaction mixture decomposed. ^{1}H NMR revealed a complex set of vinylic signals which may have resulted from an E_2 elimination (Reference 14) of the anion to form 25. We were unable to isolate any identifiable compounds from the reaction mixture.



25

Because N,N'-dibenzyl-3,4-diaminofurazan (9c) readily condensed with oxalyl chloride, we thought it worthwhile to examine other condensation reactions more closely. Attempted reaction between 9c and cyanogen oxide to form 14c was unsuccessful. However, the synthesis of 26c was achieved when 9c was first treated with n-butyl lithium in THF at -78°C followed by addition of cyanogen oxide (3). Dioxime 14c was isolated in good yield as a mixture of oxime conformers. Ring closure proceeded as expected using sodium hydroxide in ethylene glycol at 150°C for 2 hours to give 26c (Scheme 6). n-Butyl lithium was found to be the best base for the reaction.

SCHEME 6



9

14

26

R

- a = isopropyl
- c = benzyl
- d = p-methoxybenzyl
- e = tosyl
- f = (p-dimethylaminophenyl)benzyl

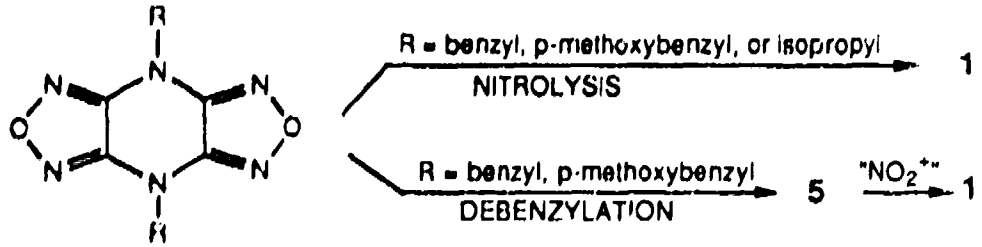
Other bases that were tried, but which gave poor results, were sodium hydride, sodium methoxide, potassium hydride, lithium diisopropylamide, potassium hexamethyl

disilazide, sodium bicarbonate, triethyl amine, and diisopropyl ethyl amine. Generation of the dianion of **9d** with n-butyl lithium followed by addition of cyanogen oxide (**3**) produced **14d** in much lower yield than corresponding **14c**. N,N'-Diisopropyl-3,4-diaminofurazan **9a** was converted to **14a**, but again in much lower yield than **9c**. This result is most likely caused by steric repulsion of the isopropyls in the anionic condensation with **3**. Note, however, that the condensation of dianions **9a** and **9d** were not always reproducible. The reason for these failures could not be determined.

Analogous condensations were tried with N,N'-ditosyl-3,4-diaminofurazan (**9e**). The tosyl group was thought to be useful because if condensation occurred to give **14e** followed by dehydration to **26e**, the tosyl groups could be nitrolyzed to the nitramine **1** or removed to yield the free amine **5**. Ditosylate (**9e**) was made by addition of tosyl chloride to **2** (Reference 15) in pyridine at 0°C. The crude reaction mixture contained a mixture of tosylates. N,N'-Ditosyl-3,4-diaminofurazan was isolated only after repeated recrystallization from ethanol. Condensation of **9e** with cyanogen oxide proved to be extremely difficult. A number of bases were used which resulted in decomposition of **9e**. A small amount of **14e** was formed when 2,2,6,6-tetramethylilithiopiperadide was used. However, **14e** was difficult to purify and obtain in any reasonable quantity.

A similar strategy was attempted by affixing silyl groups to **2**. If a 1,4-disilyl derivative of **26** could be formed, then direct nitration might be accomplished by treatment with nitronium tetrafluoroborate (Reference 16). However, efforts to attach a trimethylsilyl, tert-butyldimethylsilyl, or a tert-butyldiphenylsilyl (Reference 17) group to **2** failed.

With a number of 1,4-disubstituted difurazanopiperazines in hand, we began investigating their conversion to the target nitramine **1**. Because **26c** was the

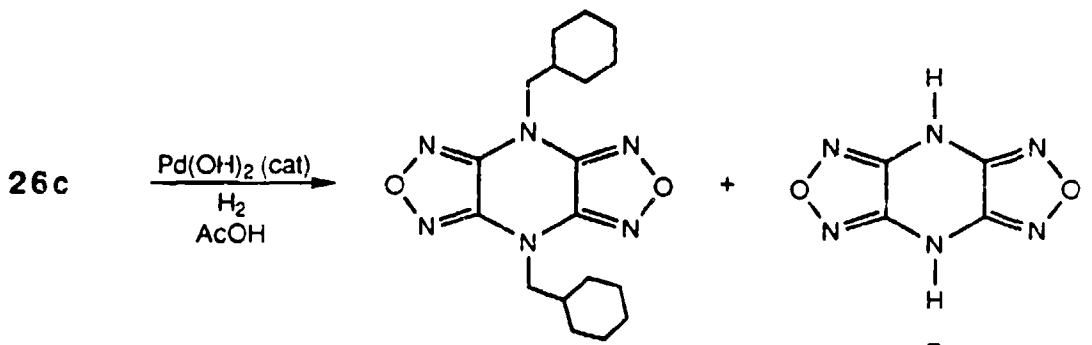


26a, c, d

a R = i-C_3H_7
c R = $C_6H_5CH_2$
d R = 4-$CH_3OC_6H_4CH_2$

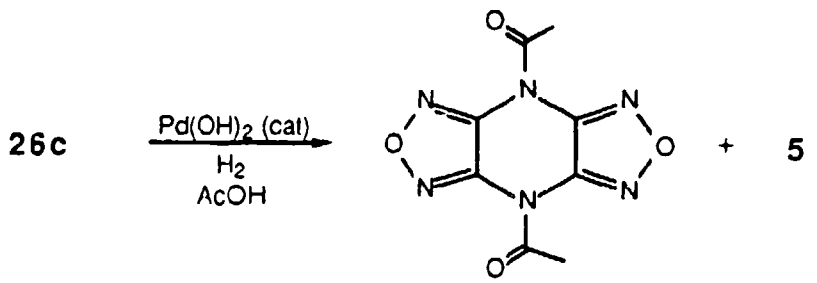
easiest to synthesize, we chose to investigate this compound first. Difurazan **26c** was seen as a protected amine. If debenzylation (Reference 5) could be achieved, the parent amine **5** could then be nitrated to the nitramine **1**. Unfortunately, **26c** showed no evidence of debenzylation using Pd/C in ethyl acetate, methanol, or acetic acid. Platinum oxide (PtO_2) in acetic acid was more encouraging. After 1 to 2 weeks under hydrogen at 50 psi, the parent amine **5** may have formed as evidenced by a broad singlet in the ^1H

NMR spec-trum at 7.0 ppm (acetone d-$_6$). Also in the reaction mixture was a significant amount of **28**. There was a competition between the desired hydrogenolysis of the benzyl groups and hydrogenation of the aromatic ring. Attempts to purify the mixture resulted in isolation of **28** and loss of **5**. Using recrystallization and chromatography methods, we failed to isolate a pure sample of **5** which appeared to be labile under the conditions employed.



28 **5**

Because PtO_2 was not adequate, the catalyst was changed to $Pd(OH)_2$ in acetic acid. As before, the hydrogenolysis required a lengthy reaction period of at least 2 weeks at 50 psi of H_2. The reaction yielded a mixture of at least two different compounds which we believe to be the amine **5** and the bis-acetyl derivative **29**. The ^1H NMR (acetone d-$_6$) showed a

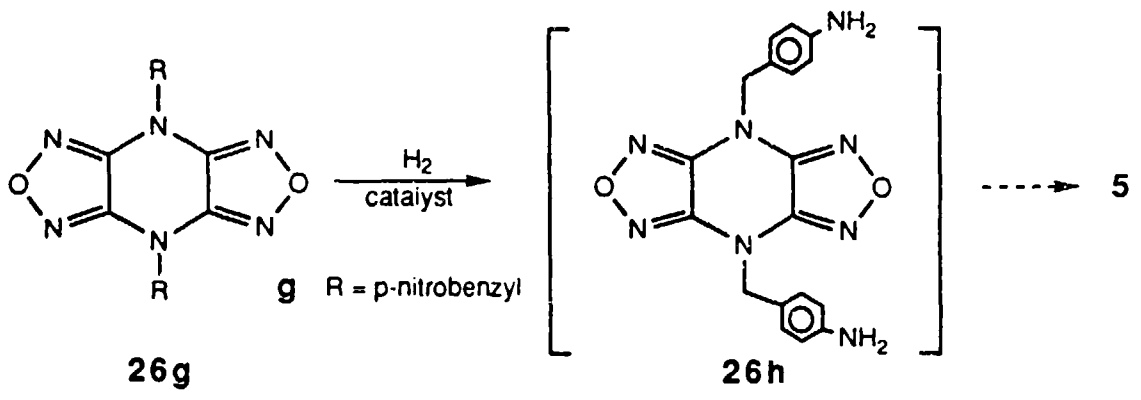


29

broad singlet at 7.0 ppm for the amine and a sharp singlet at 2.0 ppm for the diacetyl methyl hydrogens. Further evidence for **29** was the infrared (IR) spectrum which showed a carbonyl absorption at 1700 cm^{-1} (KBr) and an M^+ at 250 in the mass spectrum (molecular weight of **29** is 250). The crude reaction mixture once again was difficult to separate. We were unable to purify the individual components. Addition of electron-donating substituents to the phenyl ring, i.e., p-methoxy (**26d**), or increasing the reaction temperature, failed to improve the hydrogenolysis. Efforts to attach a different electron donating group to the ring such as p-dimethylamino as outlined in Scheme 8 failed. Although the properly substituted diaminofurazan could be made, the

yield was very low after laborious purification. Another route to attach an electron-donating amine group is also shown in Scheme 9. The nitro groups of **26g** attached to the phenyl ring should reduce readily with hydrogen/catalyst to amino groups (forming

SCHEME 9



26g **26h**

26h) which would possibly activate the ring toward hydrogenolysis. Unfortunately, as with the dimethylamino group (**9f**), the substituted furazan formed only in very low yield making both of these routes unviable.

Other methods of debenzylation that were attempted on **26c** and **d** which also failed were 2,2,2-trichloroethylchloroformate/$NaHCO_3$ in chloroform (Reference 18), $NaH_2PO_2/Pd(OH)_2$ (Reference 19), ammonium formate/Pd/C (Reference 20), and photolysis (Reference 21).

The resistance to hydrogenolysis is perplexing. In an effort to gain a better understanding of this problem, an X-ray crystal structure was obtained of **26c**. Suitable crystals for analysis were grown from ethyl acetate. Figure 2 shows the result. A model of **26c** predicts the piperazine nitrogens to be pyramidal. However, as seen from the X-ray structure, this is not the case. With the exception of the benzene rings, the molecule is entirely planar. Clearly, the strong electron withdrawing effects of the furazan rings delocalizes the electron pairs of the piperazine nitrogens. These amide-like nitrogens no longer resemble sp^3 hybridization, but rather sp^2, which accounts for the lack of reactivity (Reference 22).

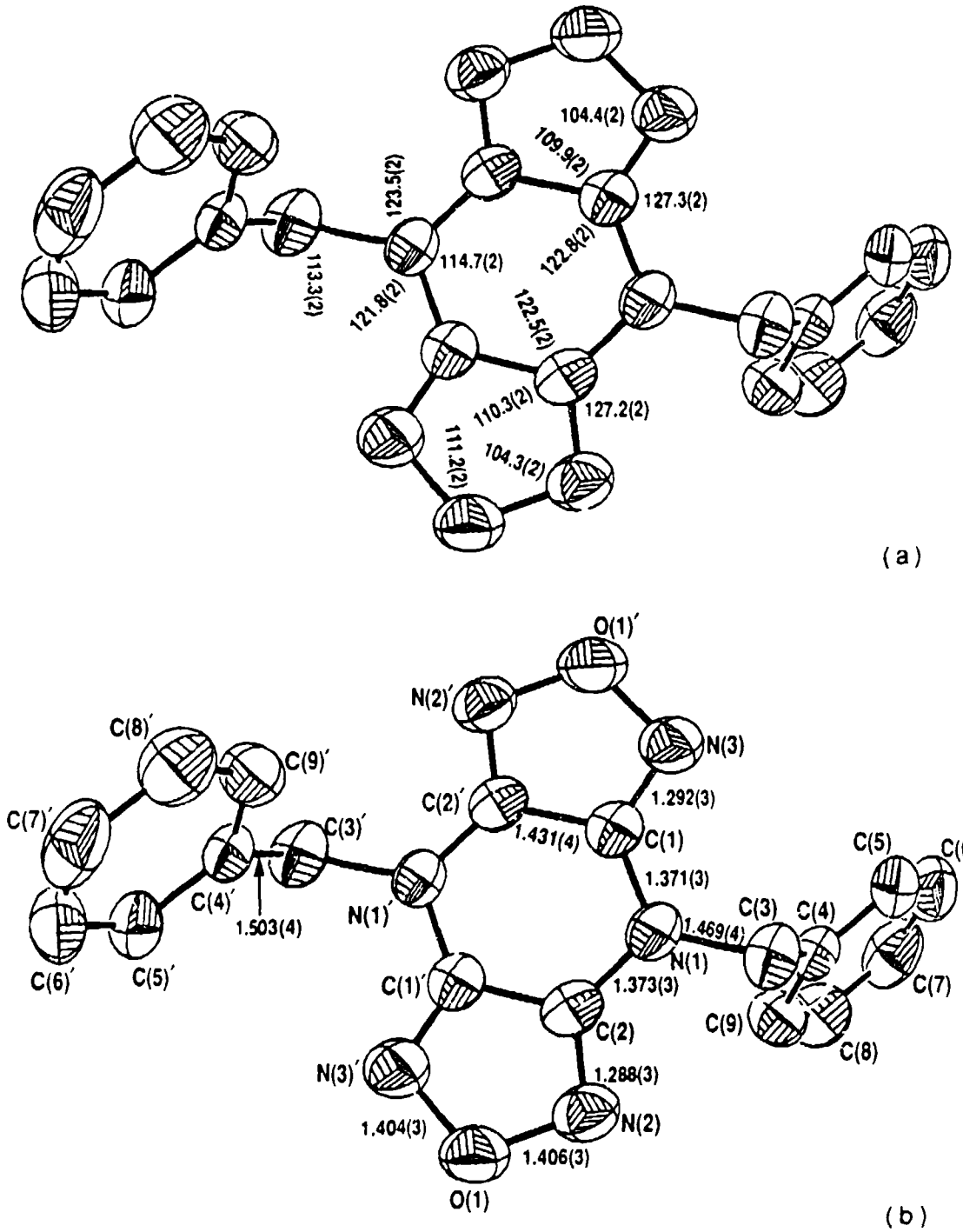
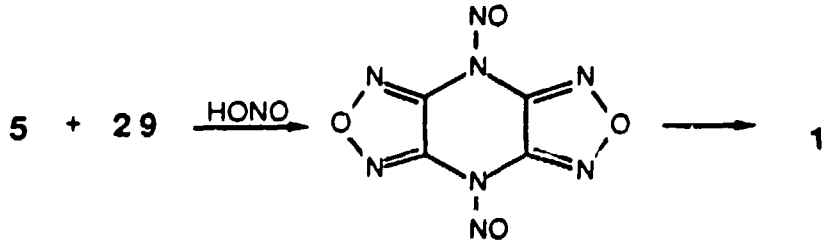


FIGURE 2. X-Ray Structure of **26c**: (a) Bond Angles and (b) Bond Lengths and Atom Numbers. Hydrogen atoms have been omitted for clarity.

Since a mixture of the amine **5** and diamide **29** was thought to be available, although in poor yield and purity, a number of nitration/nitrolysis experiments were conducted in an effort to isolate the target nitramine **1**. When the crude reaction mixture of the debenzylation of **26c**, which may have contained **5** and **29**, was treated with 25% N_2O_5/HNO_3 at 0°C, an off-white amorphous solid resulted which detonated upon impact using a simple hammer and anvil test. The mass recovery of material was low and a pure sample of any one compound could not be obtained. Attempts to purify the mixture using chromatography (silica gel, florisil, HPLC reverse phase C-18) and recrystallization all failed. The crude amine/amide mixture was also treated with nitronium tetrafluoroborate in acetonitrile. As before, no identifiable products were isolated from the complex reaction mixture. Similar results were found when the acetate/amine mixture was treated with nitrous acid in an effort to generate the nitrosoamime (**30**) which might then be oxidized to the target nitramine as illustrated.



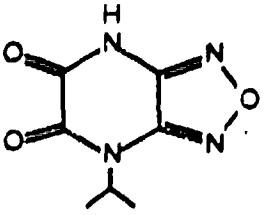
30

Direct nitrolysis of **26c** was also attempted. When **26c** was treated with N_2O_5/HNO_3 the reaction mixture turned dark blue in color. Upon quenching with ice and neutralizing with $NaHCO_3$, no identifiable products were found. Decomposition also occurred with **26d** when treated with N_2O_5/HNO_3.

Numerous nitrolyses were also tried on **26a**. Although literature precedent exists for such transformations (Reference 9), we were unsuccessful in all attempts. Reagents which were tried under a variety of conditions were

1. 100% HNO_3,
2. 100% HNO_3/NH_4NO_3/acetic anhydride, and
3. 25% N_2O_5/HNO_3.

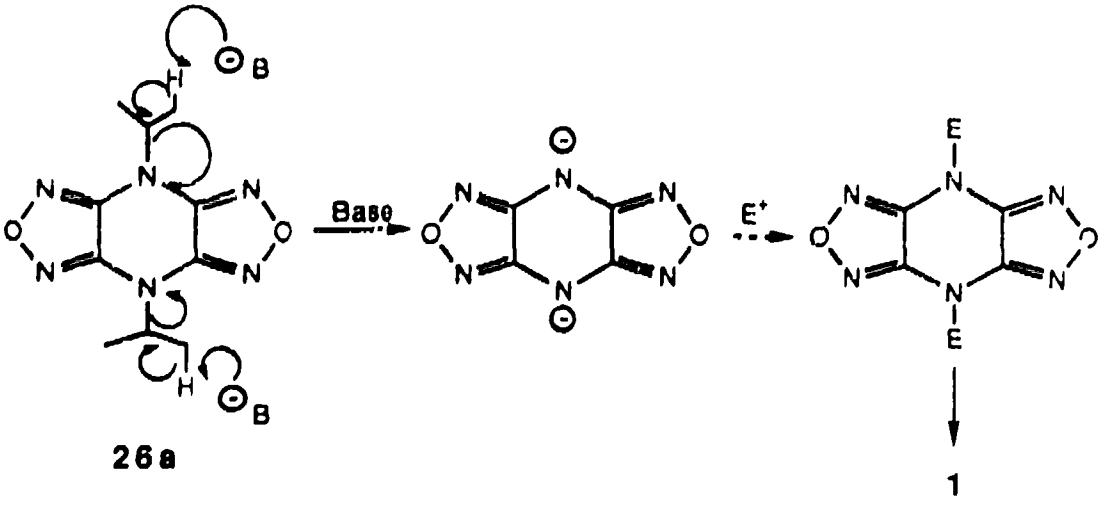
The only products isolated from these reactions were unreacted starting material and small amounts of the diketone **31**. The reactions were quenched with water, which probably hydrolyzed **26a** to **31**.



31

Since the piperazine nitrogens of this system resemble sp^2 hybridization in an electron-poor environment, it was thought possible to form nitrogen anions. This was seen as a way to further derivatize **26**. Using **26a** as starting material, the route shown in Scheme 10 was investigated. If **26a** were treated with a strong base, i.e.,

SCHEME 10

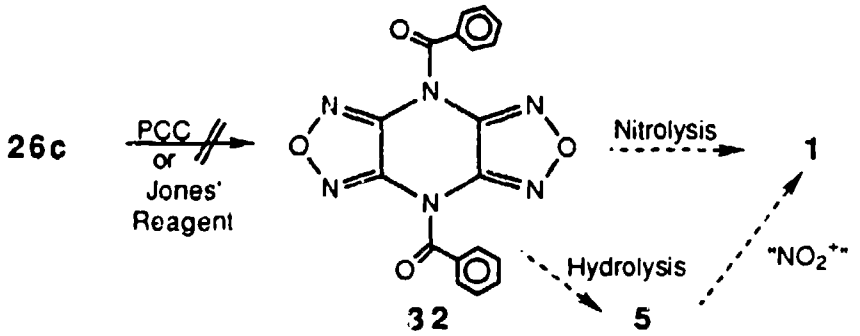


26a **1**

alkyl lithium, we believed an E_2 type of elimination would occur as shown above. The resulting double N anion could then be quenched with an electrophile. Our first choice of electrophile was a chlorosilane. If an N-silyl derivative were synthesized, treatment with nitronium tetrafluoroborate (Reference 16) should yield the desired nitramine **1**. Compound **26a** proved to be inert to n-butyl lithium. A reaction occurred only when tert-butyl lithium was used in a ten-fold excess in THF, HMPA, and TMEDA at -78°C. Attempted silylation using trimethylsilyl chloride, tert-butyldimethylsilyl chloride, or tert-butyldimethylsilyl triflate failed to yield the desired product. We believe a reaction did take place because no starting material was recovered and the ^1H NMR spectrum of the crude reaction mixture exhibited the 7.0 ppm signal (acetone) which we assigned to the parent amine. Efforts to isolate the amine led to decomposition. This route was not pursued further.

Another attempt to synthesize nitramine **1** is outlined in Scheme 11. As seen here, if **26c** could be oxidized to the dibenzoyl derivative **32** then two alternate pathways to **1** would be available. Either direct nitrolysis or hydrolysis followed by nitration would yield **1**. Unfortunately, all oxidation attempts failed. Using pyridinium

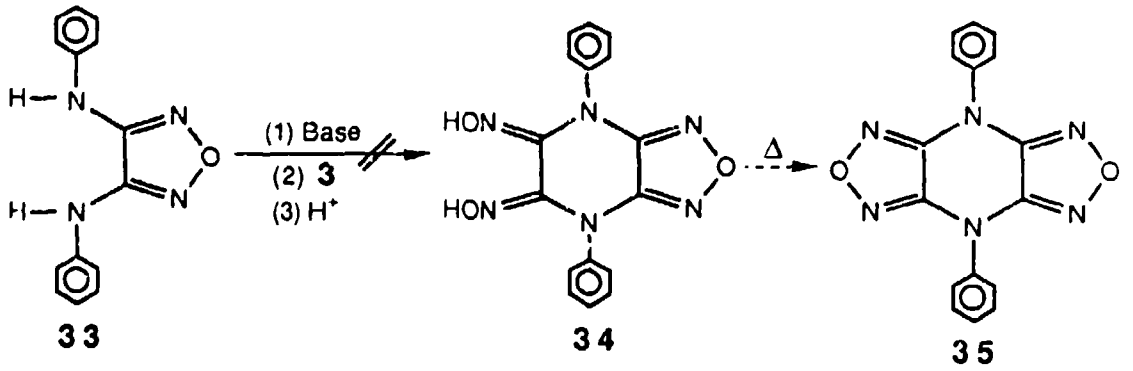
SCHEME 11

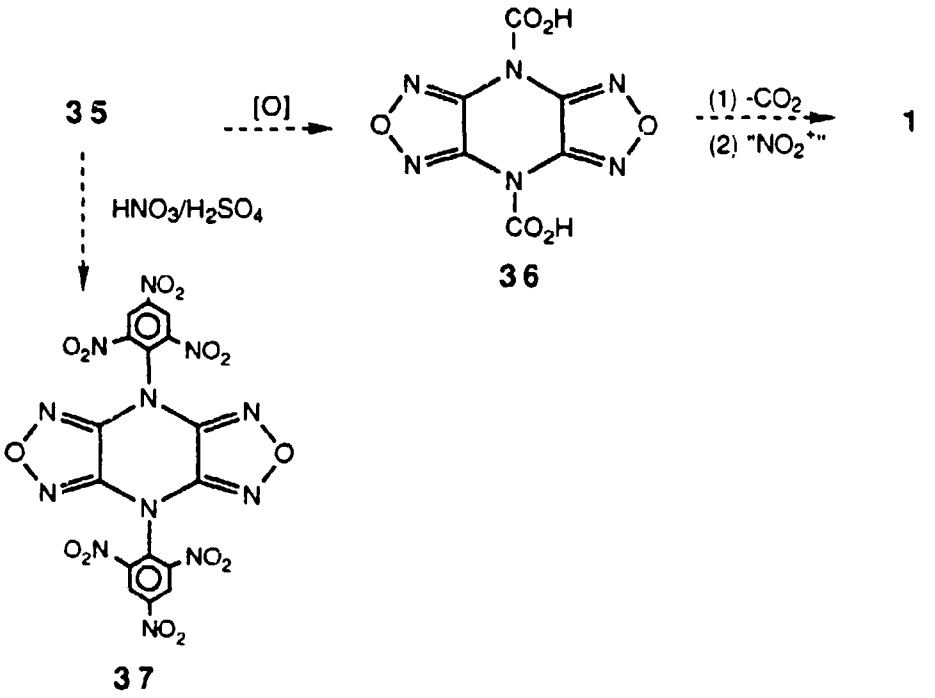


chlorochromate (Reference 23) or Jones' reagent (Reference 24) yielded only unreacted starting material.

We also attempted to generate **1** as seen in Scheme 12. Dianilinofurazan (**33**) (Reference 25) when treated with base followed by cyanogen oxide (**3**) was expected to

SCHEME 12

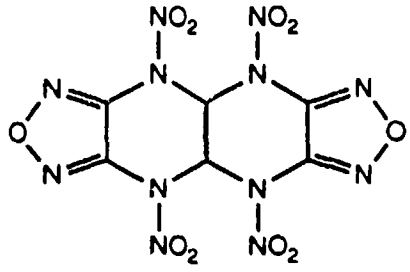




yield dioxime **34**. Subsequent dehydrative ring closure would give difurazanopiperazine **35**. This compound when oxidized with OsO_4 or RuO_2 should give diacid **36** which upon decarboxylation/nitrolysis would yield **1**. An alternative treatment for **35** would be conversion to **37** via direct nitration. However, no condensation was observed between **33** and **3**. A wide variety of bases and reaction conditions were attempted with no sign of success.

SUMMARY

This work has resulted in the synthesis of a new ring system, 1,4-disubstituted[3,4-b]-[3,4-e]difurazanopiperazine, a direct precursor to the very energetic dinitramine 1,4-dinitro[3,4-b]-[3,4-e]difurazanopiperazine. However, attempted conversion of a number of promising precursors to the highly desirable nitramine **1** was unsuccessful. Based on our results, compound **1** and its precursor diamine **5** appear to be acid-sensitive, labile substances. Similar difurazans have demonstrated acid sensitivity. The tetranitramine 1,4,5,8-tetranitro-1,4,5,8-tetraazadifurazano-[3,4-c]-[3,4-h]decalin, **38**, readily decomposes on standing in the presence of atmospheric moisture (Reference 26). This result, in addition to our work, may indicate that very electron deficient difurazans are simply too hydrolytically unstable to be of any practical use as energetic materials.



38

EXPERIMENTAL SECTION

Melting points were determined in capillary tubes with a Buchi 510 melting point apparatus. Infrared spectra were recorded with a Perkin-Elmer 137, 1330, or a Nicolet 7199 Fourier transform instrument. Proton and carbon magnetic resonance spectra were recorded with a Nicolet WB200 or IBM NR80 instrument. High pressure liquid chromatography (HPLC) analyses were done on a Perkin-Elmer Series 400 liquid chromatograph using C-18 reverse phase columns. Elemental analyses were done by Galbraith Laboratories of Knoxville, Tenn. Mass spectra were recorded on a Hewlett-Packard Model 5985 instrument. Exact mass spectra analyses were done by the University of California, Riverside Mass Spectroscopy Center.

GENERAL PROCEDURE FOR THE PREPARATION OF SUBSTITUTED AMINO GLYOXIMES **5** AND **8**

The appropriate amine (4 eq) and dichloroglyoxime (1 eq) were mixed in THF. A thick precipitate immediately formed. The resulting slurry was refluxed for 2 hours, cooled, and the amine salts were separated by filtration. The solvent of the mother liquor was removed under reduced pressure to yield the crude substituted amino glyoximes as yellow solids which were recrystallized from ethanol/water mixtures. Properties of the four compounds synthesized are given below.

N,N'-Diisopropyldiaminoglyoxime (8a)

^{1}H NMR (acetone) δ 8.95 (br s, 2 H), 5.09 (d, J = 9.7 Hz, 2 H), 3.62 (m, 2 H), 1.14 (d, J = 6.4 Hz, 12 H); ^{13}C NMR 147.7, 45.1, 24.5; IR (KBr) 3550, 3200 (broad), 2950, 1650, 1610, 1450, 1370, 1150; mp 210 to 212°C. Analysis calculated for $C_8H_{18}N_4O_2$: C, 47.50; H, 8.97; N, 27.71. Found: C, 47.46; H, 9.00; N, 27.45.

N,N'-Dicyclohexyldiaminoglyoxime (8b)

^{1}H NMR (DMSO) δ 9.50 (s, 2 H), 5.34 (d, J = 9.9 Hz, 2 H), 3.05 (br, s, 2 H), 1.75 (m, 20 H); ^{13}C NMR 24.7, 24.8, 34.3, 51.0, 146.5; IR (KBr) 3300 (broad), 2900, 1630, 1475, 1425, 1140, 960, 930; mp 209 to 211°C. Analysis calculated for $C_{22}H_3ON_4O_2$: C, 69.08; H, 7.91; N, 14.65. Found: C, 69.12; H, 7.88; N, 14.61.

N,N'-Diisopropyl-N,N'-dibenzyldiaminoglyoxime (12a)

^{1}H NMR (acetone) δ 9.3 (br s, 2 H), 7.3 (m, 10 H), 4.38 (d, J_A = 15.6, 2 H), 4.14 (d, J_B = 15.6, J_{AB} = 19.2, 2 H), 3.68 (septet, J = 6.7, 2 H), 1.06 (d, J_A = 6.7, 6 H), 1.19 (d, J_B = 6.7, J_{AB} = 25, 6 H); IR (KBr) cm^{-1} 3320, 2900, 1625, 1450, 1370, 1175, 980, 935; mp 133 to 135°C. Analysis calculated for C, 69.08; H, 7.91; N, 14.65. Found: C, 69.12; H, 7.88; N, 14.61.

N,N'-Dicyclohexyl-N,N'-dibenzyldiaminoglyoxime (12b)

^{1}H NMR (acetone) splitting patterns are apparent, δ 7.93 (s, 2 H), 7.25 (m, 10 H), 4.35 (d of d, AB quartet, J_A = 15.5 Hz, J_{AB} = 51.6 Hz 4 H), 3.31 (m, 2 H), 1.4 (m, 20 H); IR (KBr) 3350, 3050, 2900, 1640, 1450, 1050, 940; mp 155 to 157°C. Analysis calculated for $C_{28}H_{38}N_4O_2H_2O$: C, 69.96; H, 8.40; N, 11.66. Found: C, 70.29; H, 8.52; N, 11.91.

PREPARATION OF N,N'-DIISOPROPYL-3,4-DIAMINOFURAZAN (9a)

Sodium borohydride (15.2 g, 400 mmol) was added in portions over 1/2 hour to a stirring solution of 3,4-diaminofurazan (2.0 g, 20 mmol) in acetone (40 mL) and glacial acetic acid (120 mL) at 0°C. The resulting thick white slurry was slowly allowed to warm to ambient temperature and stirred a total of 18 hours. Water (250 mL) was added, and the clear solution was extracted with ethyl acetate (3 x 100 mL). The combined organic layers were neutralized with solid sodium bicarbonate, washed with water (100 mL), brine (100 mL), and dried ($MgSO_4$). Solvent was removed under reduced pressure to afford crude **9a** as an oily white solid which was recrystallized from ethyl acetate/hexane (2.17 g as white needles, mp 83 to 85°C, 59% yield). ^{1}H NMR (acetone) δ 5.1 (br s, 2 H), 3.61 (m, 2 H), 1.19 (d, J = 6.4 Hz) 12 H; ^{13}C NMR 149.1, 45.8, 21.8; IR (KBr) 3300, 2950, 1600, 1575, 1370, 1175, 820. Analysis calculated for $C_8H_{16}N_4O$: C, 52.14; H, 8.77; N, 30.41. Found: C, 51.90; H, 8.72; N, 30.28.

PREPARATION OF N,N'-DIBENZYL-3,4-DIAMINOFURAZAN (9c)

3,4-Diaminofurazan, **2**, (2 g, 20 mmol), benzaldehyde (4.1 mL, 40 mmol), and p-toluenesulphonic acid (10 mg) were mixed in benzene and heated at reflux under nitrogen in a Dean-Stark apparatus for 18 hours. The yellow solution was then cooled to ambient temperature and solvent was removed under reduced pressure. The oily yellow solid was dissolved in THF (100 mL) and methanol (30 mL); sodium borohydride (6 g) was carefully added over a period of 20 minutes to the stirring solution at room temperature. Once the addition was complete, the resulting mixture was stirred for 18 hours then quenched with 1 M HCl (100 mL) and extracted with ethyl acetate (3 x 50 mL). The organic layers were combined and washed with water (100 mL), saturated sodium chloride (50 mL), and dried ($MgSO_4$). The solvent was removed under reduced pres-sure to yield a white oily solid which was recrystallized from ethyl acetate/hexane to afford 4.1 g of the desired material as white needles (mp 109 to 111°C, 73% yield). ^1H NMR (200 MHz, $CDCl_3$) 7.28 (s, 10 H), 4.31 (d, J = 5.1 Hz, 4 H) 4.13 (br s, 2 H); ^{13}C NMR 149.8, 137.5, 128.6, 127.9, 127.7, 48.7; IR (KBr) 3370, 3300, 3027, 2921, 1620, 1594, 1495, 1253, 742, 700. Analysis calculated for $C_{16}H_{16}N_4O$: C, 68.55; H, 5.75; N, 19.99. Found: C, 68.64; H, 5.78; N, 19.95.

PREPARATION OF 3,4-BIS(p-METHOXYBENZYLANILINO)-3,4-DIAMINOFURAZAN (9d)

Preparation for **9d** is the same as for **9c** (22% yield). ^1H NMR (200 MHz, acetone d-$_6$) δ 7.29 (d, J_A = 8.5, 4 H), 6.85 (d, J_B = 8.5, 4 H), (J_{AB} = 87.6), 4.6 (br s, 2 H), 4.32 (d, J = 8.5, 4 H), 3.75 (s, 6 H); ^{13}C NMR 160.0, 150.6, 131.5, 130.1, 114.6, 55.2 48.4; IR (KBr) cm^{-1} 3420, 3000, 2920, 1620, 1560, 1500, 1260, 1060, 810; mp 149 to 151°C. Analysis calculated for $C_{18}H_{20}N_4O_2$: C, 63.50; H, 5.93; N, 16.46. Found: C, 63.43; H, 6.04; N, 16.46.

PREPARATION OF N,N'-(p-TOLUENESULFONYL)-3,4-DIAMINOFURAZAN (9e)

Tosyl chloride (3.82 g, 20 mmol) in dry pyridine (20 mL) was added dropwise to a stirring solution of 3,4-diaminofurazan (1 g, 10 mmol) in dry pyridine (20 mL) at 0°C under N_2, resulting in a yellow mixture which was slowly warmed to ambient temperature and stirred overnight. The yellow suspension was then poured into H_2O (50 mL) and extracted into ethyl acetate (3 x 50 mL). Organic layers were combined and washed with H_2O (75 mL), saturated sodium chloride (50 mL), dried ($MgSO_4$), and solvent removed under reduced pressure to yield a yellow oil and solid which was recrystallized from 95% ethanol (3 x) to yield 610 mg of **9e** (15%, mp 136 to 138°C) as white crystals.

^1H NMR (acetone d-$_6$) δ 7.5 m (AA'BB' pattern) 8 H, 5.5 (br s 2 H), 2.40 (s 6 H); ^{13}C NMR (acetone d-$_6$) 156.4, 147.4, 135.6, 130.7, 129.7, 21.6; IR (KBr) 3420, 3100, 2910, 1630, 1590, 1390, 1120, MS 408 (M^+), 153 (100%), 91.

Analysis calculated for $C_{16}H_{16}N_4O_5S_2$: C, 47.04; H, 3.96; N, 13.72. Found: C, 46.64; H, 3.94; N, 13.65.

PREPARATION OF 1,4-DIBENZYL-5,6-DIKETO[3,4-b]FURAZANOPIPERAZINE (16c)

N,N'-Dibenzyl-3,4-diaminofurazan (100 mg, 0.4 mmol) in dry benzene (10 mL) was added via a syringe pump to a stirring solution of oxalyl chloride (0.05 mL, 0.5 mmol) and sodium bicarbonate in dry benzene (20 mL) at ambient temperature under nitrogen over 13 hours. Once the addition was complete, the resulting solution was stirred an additional 5 hours. Solvent was removed under reduced pressure. Water (10 mL) was added to the residual solid and then extracted with ethyl acetate (3 x 15 mL). The combined organic layers were washed with water (10 mL), brine (10 mL), and dried ($MgSO_4$). Solvent was removed under reduced pressure to afford 100 mg of **16c** (mp 189 to 190°C, 75% yield) as a light yellow solid which could be further purified by recrystallization from ethyl acetate/hexane. ^1H NMR ($CDCl_3$) δ 7.6 (m, 10 H), 5.19 (s, 4 H); ^{13}C NMR 151.7, 143.5, 133.3, 129.7, 129.0, 128.9, 48.7; IR ($CHCl_3$) 3020, 1720, 1590, 1320, 1210, 1200, 690, 670. Analysis calculated for $C_{18}H_{14}N_4O_3$: C, 64.66; H, 4.22; N, 16.76. Found: C, 64.62; H, 4.21; N, 16.76.

PREPARATION OF 1,4-DINITROSO[3,4-b]FURAZANOPIPERAZINE (21)

Concentrated HCl (4 mL) was added dropwise to a stirring solution of furazano-[3,4-b]piperazine, **20** (1.0 g, 8 mmol), and sodium nitrite (1.24 g, 18 mmol) in H_2O (50 mL) at 60°C. A thick yellow solid formed, which was stirred at 60°C for 50 minutes and then cooled to 0°C for an additional 45 minutes, collected by suction filtration, and recrystallized from warm benzene to yield 1.0 g of 1,4-dinitroso-furazano[3,4-b]piperazine as yellow plates (mp 93 to 95°C, 68% yield). ^1H NMR (200 MHz) in acetone d-6, broad singlet at 4.29 ppm (major conformer), two minor conformers seen as broad singlets at 5.20 and 4.49 ppm; ^{13}C NMR (acetone d-6, major conformer) 39.28, 144.51 ppm; IR (KBr) cm^{-1} 3000 (w), 1630 (s), 1560 (s), 1500 (s), 1400 (s), 1350 (s), 1075 (s). Analysis calculated for $C_4H_4N_6O_3$: C, 26.09; H, 2.19; N, 45.65. Found: C, 26.08; H, 2.25: N, 45.72.

PREPARATION OF 1,4-DIBENZYL-5,6-DIOXIMINO[3,4-b]FURAZANOPIPERAZINE (14c)

n-Butyl lithium (1.6 M in hexane, 21.6 mL, 35 mmol) was added dropwise to a stirring solution of N,N'-dibenzyl-3,4-diaminofurazan, **9c** (2.42 g, 8.6 mmol), in THF (100 mL) at -78°C under nitrogen. After 1 hour, dichloroglyoxime (1.35 g, 8.6 mmol) in THF (25 mL) was added rapidly in one portion, also at -78°C. The solution immediately turned dark red orange in color. After stirring 1 hour at -78°C and 2 hours at room temperature, the dark red solution was poured onto 1 M NaH_2PO_4 (100 mL) and extracted into ethyl acetate (3 x 50 mL). The combined organic layers

were washed with water (100 mL), brine (100 mL), and dried ($MgSO_4$). Solvent was removed under reduced pressure to afford **10** as a light yellow solid which was recrystallized from warm benzene (1.3 g, 42% yield, mp 185 to 186°C). ^1H NMR (DMSO) mixture of conformers, δ 11.93 (s), 11.82 (s), 11.78 (s (very small)), 7.31 (br s), 5.29 (s), 4.98 (s); IR (KBr) 3200 br, 1650, 1600, 1490, 1440, 1360, 1060, 950, 840; Mass Spec 364 (M^+), 347 (-OH), 346 ($-H_2O$), 91 (100%). Analysis calculated for $C_{18}H_{16}N_6O_3$: C, 59.33; H, 4.43; N, 23.07. Found: C, 59.35; H, 4.42; N, 23.10.

PREPARATION OF 14d

Preparation of **14d** is the same as for **14c.** ^1H NMR (80 MHz, acetone d-6) 2 conformers seen δ 12.0 (br s, 2 H), 7.25 (m), 6.75 (m), 5.38 (s), 4.87 (s), benzyl $-CH_2-$, 3.67 (s, $-OCH_3$); IR (KBr) cm^{-1} 3200, 3005, 2950, 1595, 1510, 1380, 1260; mp 195 to 197°C. Exact mass (chemical ionization using isobutane) calculated, 425.1573; found, 425.1567.

PREPARATION OF 1,4-DIISOPROPYL-5,6-DIOXIMINO[3,4-b]FURAZANOPIPERAZINE (14a)

n-Butyl lithium (1.6 M in hexane, 20.3 mL, 32.6 mmol) was added dropwise to a stirring solution of N,N'-diisopropyl-3,4-diaminofurazan (**17**) (1.50 g, 8.2 mmol) in THF (75 mL) at -78°C under nitrogen. After 1 hour, dichloroglyoxime (1.27 g, 8.2 mmol) in THF (15 mL) was added rapidly in one portion. The solution immediately turned dark red in color. After stirring 1 hour at -78°C and 2 hours at ambient temperature, the dark red-brown solution was poured onto 1 M NaH_2PO_4 (100 mL) and extracted into ethyl acetate (3 x 50 mL) The combined organic extracts were washed with water (100 mL), brine (100 mL), and dried ($MgSO_4$). Solvent was removed under reduced pressure to give **18** as a dark yellow solid which was recrystallized from warm benzene (0.45 g, 20% yield, mp 151 to 153°C). ^1H NMR (acetone) δ 12.0 (br s, 2 H), 4.6 (septet, J = 6.4 Hz, 2 Hz), 1.41 (d, J = 6.4 Hz, 12 H); IR (KBr) 3200 (broad), 2900, 1650, 1600, 1560, 1450, 1370, 1040, 930, 910; exact mass calculated, 268.1284; found, 268.1277.

PREPARATION OF 1,4-DIBENZYL[3,4-b]DIFURAZANOPIPERAZINE (26c)

1,4-Dibenzyl-5,6-dioximinofurazanopiperazine (**14c**) (1.14 g, 3.1 mmol) was added in one portion to a stirring solution of sodium hydroxide (0.12 g, 3.1 mmol) in ethylene glycol (10 mL) at 150°C. After 2 hours, the solution was cooled and water (20 mL) was added. There was an immediate formation of precipitate. After cooling to 0°C for 1 hour, **26c** was collected by vacuum filtration as an off-white solid (0.60 g, 56% yield, 93% yield based on recovered starting material, mp 170 to 175°C, dec). After the mother liquor stood for 3 days, a white solid (0.46 g), starting material (**14c**), was recovered. ^1H NMR (acetone) δ 7.5 (m, 10 H), 5.02 (s, 4 H); ^{13}C NMR

148.7, 135.3, 129.6, 129.5, 129.2, 52.5; IR (KBr) 3000, 2990, 1640, 1600, 1390, 1350, 960; Mass Spec 346, 91 (100%). Analysis calculated for $C_{18}H_{14}N_6O_2$: C, 62.41; H, 4.08; N, 24.27. Found: C, 62.29; H, 4.11; N, 24.12.

PREPARATION OF 1,4-DIISOPROPYL[3,4-b]DIFURAZANOPIPERAZINE (26a)

1,4-Diisopropyl-5,6-dioximinofurazanopiperazine (18) (0.28 g, 1.04 mmol) was added in one portion to a stirring solution of sodium hydroxide (42 mg, 1.04 mmol) in ethylene glycol (5 mL) at 150°C. After 2 hours at 150°C, the solution was cooled to ambient temperature, water (10 mL) was added, and the resulting slurry cooled to 0°C for 1 hour. 1,4-Diisopropyldifurazanopiperazine was collected by vacuum filtration as an off-white solid (190 mg, 73% yield, mp 159 to 161°C). ^{1}H NMR (acetone) δ 4.45 (septet, J = 6.4 Hz, 2 H), 1.40 (d, J = 6.4 Hz, 12 H); ^{13}C (acetone) 147.8, 53.2, 18.4; IR (KBr) 2900, 1625, 1590, 1370, 1050, 820; Mass Spec 250 (M^+), 166 (100%). Exact mass calculated, 250.1178; found, 250.1188.

PREPARATION OF 1,4-p-METHOXYBENZYL-[3,4-b]-[3,4-e]-DIFURAZANOPIPERAZINE (26d)

The preparation of **26d** is the same as for **26c** (70% yield). ^{1}H NMR (80 MHz, DMSO d-6) δ 7.55 (d, (J_A = 10, 4 H), 6.95 (d, J_B = 10, J_{AB} = 32, 4 H), 4.90 (s, 4 H), 3.70 (s, 6 H); ^{13}C 159.0, 147.2, 129.3, 125.6, 113.8, 54.8, 50.6; IR (KBr) cm^{-1} 3020, 2910, 1580, 1505, 1250, 1175, 1030, 810; mp 187 to 188°C. Exact mass calculated, 406.1389; found, 406.1382.

PREPARATION OF 1,4-CYCLOHEXYLMETHYLENE-[3,4-b]-[3,4-e]-DIFURAZANOPIPERAZINE (28)

1,4-Dibenzyl[3,4-b]-[3,4-e]difurazanopiperazine (**26c**) (230 mg, 0.7 mmol) was dissolved in glacial acetic acid (10 mL). Platinum oxide (10 mg) was added and the mixture was placed on a Parr hydrogenation apparatus at room temperture, 50 psi hydrogen pressure for 4 days. The mixture was celite filtered and partitioned between $CHCl_3$ (100 mL) and H_2O (30 mL). The $CHCl_3$ layer was neutralized with aqueous sodium bicarbonate, washed with brine (25 mL), and dried ($MgSO_4$). Solvent was removed under reduced pressure yielding an off white solid (175 mg), which was purified by silica gel chromatography (eluted with 30% ethyl acetate-hexane). Compound **28** was isolated as a white solid (50 mg, 20%). ^{1}H NMR (80 MHz, $CDCl_3$) δ 3.71 (d, J = 7.2, 4 H), 2.2 (m, 2 H), 1.75 (m, 10 H), 1.2 (m, 10 H); ^{13}C NMR 147.1, 54.6, 35.1, 30.5, 26.1, 25.5; IR (CH_2Cl_2) cm^{-1} 2920, 2850, 1670, 1580, 1320, 915, 870, 835; mp 222 to 223°C Analysis calculated for $C_{18}H_{26}N_6O_2$: C, 60.30; H, 7.32; N, 23.45. Found: C, 60.30; H, 7.38; H, 23.28.

REFERENCES

1. (a) L. R. Rothstein, R. Petersen, *Prop. and Explo.*, Vol. 6 (1981), pp. 91-93.
(b) Naval Surface Weapons Center. *Estimation of Normal Densities of Explosive Compounds From Empirical Atomic Volumes*, by D. A. Cichra, J. R. Holden, and C. Dickinson, Silver Spring, Md., NSWC, February 1980. 39 pp. (TR79-273, publication UNCLASSIFIED.)

2. (a) N. E. Alexandrov and D. N. Nicolaides. *J. Chem. Soc. (C)* (1969), p. 2319.
(b) C. Grundman, V. Mini, J. M. Dean, and H. -D. Fromeld. *Justus Liebig's Ann. Chem.*, Vol. 687 (1965), p. 191.
(c) D. W. Moore and R. L. Willer. *J. Org. Chem.*, Vol. 50 (1985), p. 5123.

3. (a) P. Walstra, W. P. Trompen, and J. T. Hacknann. *Recueil*, Vol. 87 (1968), p. 452.
(b) D. N. Nicolaides, K. E. Litinas, and I. Naidou. *Chim. Chron. New Series*, Vol. 11 (1982), p. 73.

4. (a) V. G. Andrianov and A. V. Eremeev. *Chem. Het. Cpds. U.S.S.R. (Eng)* (1985), p. 937.
(b) M. A. Shokhen, V. G. Andrianov, and A. V. Eremeev. *Khim. Geteotsikl. Soedin* (1979), p. 1355.

5. W. A. Hartung and R. Simonoff. *Organic Reactions, Vol. VII*, New York, John Wiley & Sons, 1953. P. 263.

6. G. W. Gribble, P. D. Cord, J. Skotnicki, S. E. Dietz, J. T. Eaton, and J. L. Johnson. *J. Am. Chem. Soc.*, Vol. 96 (1974), p. 7812.

7. A. Gasco, G. Rua, G. Menziani, G. M. Nano, and G. Tappi. *J. Heterocyclic Chem.* (1960), p. 769.

8. N. Kornblum and L. Fishbein. *J. Am. Chem. Soc.*, Vol. 77 (1955), p. 6269.

9. (a) W. P. Norris. *J. Org. Chem.*, Vol. 25 (1960), p. 1244.
(b) H. G. Adolph and D. A. Cichra. *J. Org. Chem.*, Vol. 47 (1982), p. 2474.

10. *Chemistry of the Carbon-Nitrogen Double Bond*, S. Fatai, ed., New York, John Wiley & Sons, 1970. P. 64.

11. (a) A. I. Meyers, A. Nabeya, H. W. Adickes, and I. R. Politzer. *J. Am. Chem. Soc.*, Vol. 91 (1969), p. 763.
(b) A. I. Meyers and A. Nabeya. *J.C.S. Chem. Comm.* (1967), p. 1163.

12. (a) O. Vogl and A. C. Knight. *Macromolecules*, Vol. 1, 1968, p. 311.
(b) O. Vogl and H. G. Chang. *J. Polym. Sci.*, Vol. 15, 1977, p. 311..
(c) B. Loev , J. H. Musser, R. E. Brown, H. Jones, R. Kahen, F. -C. Huang, A. Khandwala, P. Sonnino-Goldman, and M. J. Leibowitz. *J. Med. Chem.*, Vol. 28 (1985), p. 363.

13. (a) D. Seebach and D. Enders. *Angew. Chem. Int. Ed.*, Vol. 14, 1975, p. 15.
(b) A. I. Meyers, L. M. Fuentes, and Y. Kubota. *Tetrahedron*, Vol. 40, 1984, p. 1361.
(c) P. Beak, W. J. Zajdel, and D. B. Reitz. *Chem. Rev.*, Vol. 84 (1984), p. 471.
(d) A. I. Meyers and L. M. Fuentes. *J. Am. Chem. Soc.*, Vol. 105, 1983, p. 117.

14. F. Babudri, S. Florio, A. Reho, and G. Trapani. *J. Chem. Soc. Perkin Trans. I* (1984), p. 1949.

15. H. Stetter. *Chem. Ber.*, Vol. 86, 1953, p. 161.

16. R. J. Schmitt, J. C. Bottaro, R. Malhotra, and C. D. Bedford. *J. Org. Chem.*, Vol. 52, 1987, p. 2294.

17. L. E. Overman, M. E. Okazaki, and P. Mishra, *Tetrahedron Lett.* (1986), p. 4391.

18. (a) G. Just and K. Grozinger. *Synthesis* (1976), p. 457.
(b) L. E. Overman and S. R. Angle. *J. Org. Chem.*,Vol. 50, 1985, p. 4021.
(c) V. H. Rawal, R. J. Jones, and M. P. Cava, *J. Org. Chem.*, Vol. 52 1987, p. 19.

19. S. K. Boyer, J. Back, J. McKenna, and E. Jagdman. *J. Org. Chem.*, Vol. 50, 1985, p. 3408.

20. S. Ram and L. D. Spicer. *Tetrahedron Lett.* (1987), p. 515.

21. (a) J. D. Timpa, M. G. Legendre, G. W. Griffin, and P. K. Das. *Carbohydrate Research*, , Vol. 117, 1983, p. 69.
(b) N. J. Turro, C. -H. Tung, I. R. Gould, G. W. Griffin, R. L. Smith, and A. Manmade. *J. Photochem.*, Vol. 24, 1984, p. 265.
(c) A. Okamoto and D. R. Arnold. *Can. J. Chem.*, Vol. 63, 1985, p. 2340.
(d) L. W. Reichel, G. W. Griffin, A. J. Muller, P. K. Das, and S. Ege. *Can. J. Chem.*, Vol. 62, 1984, p. 424.
(e) A. J. Maroulis and D. R. Arnold. *J. Am. Chem. Soc.*, Vol. 98, 1976, p. 5931.
(f) H. F. Davis, P. K. Das, L. W. Reichel, and G. W. Griffin. *J. Am. Chem. Soc.*, Vol. 106, 1984, p. 6968.

22. M. Friefelder. *Practical Catalytic Hydrogenation*, New York, John Wiley & Sons, 1971. P. 427.

23. R. Rathore, N. Saxena, and S. Chandrasekaran. *Syn. Comm.* (1986), p. 1493.

24. R. Rangarajan and E. J. Eisenbraun. *J. Org. Chem.*, Vol. 50, 1985, p. 2435.

25. M. D. Coburn. *J. Het. Chem.*, Vol. 5, 1968, p. 83.

26. Naval Weapons Center. *Synthesis of a New Energetic Material, 1,4,5,8-Tetranitro-1,4,5,8-Tetraazadifurazano-[3,4-c][3,4-h]Decalin (CL-15)* by Rodney L. Willer. China Lake, Calif., NWC, November 1982. 32 pp. (NWC TP 6397, publication UNCLASSIFIED.)

INITIAL DISTRIBUTION

4 Naval Air Systems Command
  AIR-5004 (2)
  AIR-932 (1)
  AIR-932F (1)
10 Chief of Naval Research, Arlington (OCNR-1132, Dr. R. S. Miller)
2 Naval Sea Systems Command (Technical Library)
1 Commander in Chief, U. S. Pacific Fleet (Code 325)
1 Headquarters, U. S. Marine Corps (Code RD-1, A. L. Slafkosky, Scientific Advisor)
1 Commander, Third Fleet, San Francisco
1 Commander, Seventh Fleet, San Francisco
2 Naval Academy, Annapolis (Director of Research)
1 Naval Explosive Ordnance Disposal Technology Center, Indian Head (Code D, L. Dickinson)
2 Naval Ordnance Station, Indian Head
  Code 5253, W. G. Roger (1)
  Code 5253L, J. Moniz (1)
1 Naval Postgraduate School, Monterey (Code 012, Dr. J. Wall, Director, Research Administration)
8 Naval Research Laboratory
  Code 2627 (6)
  Code 6030, Dr. R. Gilardi (1)
  Code 6120, Dr. W. Moniz (1)
1 Naval Surface Warfare Center, Indian Head (Code R16, J. Consaga)
11 Naval Surface Warfare Center, White Oak Laboratory, Silver Sring
  Code R10, K. F. Mueller (1)
  Code R10C, L. A. Roslund (1)
  Code R10D
    H. G. Adolph (1)
    C. Bedford (1)
  Code R10E, J. M. Kelley (1)
  Code R11
    C. Gotzmer (1)
    J. M. Short (1)
  Code R13, C. Dickinson (1)
  Code R16, N. Seiden (1)
  Dr. R. Doherty (1)
  Dr. J. Holden (1)
1 Naval War College, Newport
1 Naval Weapons Support Center, Crane (Code 5063, Dr. H. Webster III)
1 Naval Weapons Station, Yorktown (L. R. Rothstein)
1 Office of Naval Technology, Arlington (Dr. E. Zimet)
4 Army Armament Research and Development Center, Dover
  SMCAR-LCE-C
    Dr. J. Alster (1)
    Dr. E. Gilbert (1)
    Dr. N. Slagg (1)
    Dr. G. Sollott (1)
5 Army Ballastic Research Laboratory, Aberdeen Proving Ground
  DRCAR-IBD, A. Junasz (1)
  DRXBR-IRD
    Director (1)
    Dr. I. W. May (1)
  DRXBR-TBD
    Dr. P. Howe (1)
    J. J. Rocchio (1)

3 Army Research Office, Research Triangle Park
  Chemical and Biological Sciences Division
    R. Ghirardelli (1)
    C. R. Husk (1)
  Engineering Division, Dr. D. Mann (1)
1 Ballistic Missile Defense Advanced Technology Center, Huntsville (D. C. Sayles)
1 Air Force Academy, Colorado Springs (FJSRL/NC, J. S. Wilkes, Jr.)
2 Air Force Astronautics Laboratory, Edwards Air Force Base
  AFAL/DY, R. Geisler (1)
  AFAL/LKLR, Dr. F. Roberto (1)
1 Air Force Intelligence Agency, Bolling Air Force Base (AFIA/INTAW, Maj. R. Esaw)
2 Air Force Office of Scientific Research, Bolling Air Force Base
  Directorate of Chemical and Atmospheric Sciences
    Dr. D. L. Ball (1)
    Dr. A. J. Matuszko (1)
12 Defense Technical Information Center, Alexandria
1 Fluorochem, Incorporated, Azusa, CA (Dr. R. D. Chapman)